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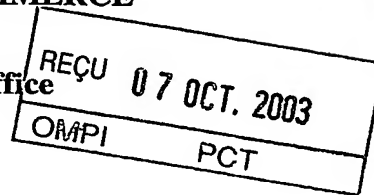
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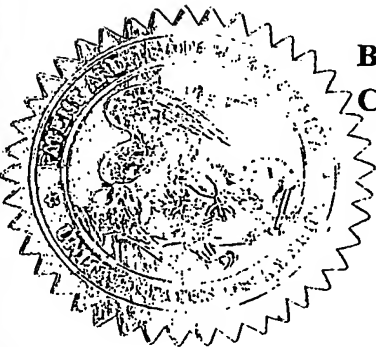
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APPLICATION NUMBER: 60/407,753

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# **PROVISIONAL APPLICATION FOR PATENT COVER SHEET** This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

INVENTOR(S)					
Given Name (first and middle (if any))		Family Name or Surname		Residence (City and either State or Foreign Country)	
Daniel L. Gordon T.		Crosby Rivers		Sugar Land, TX Houston, TX	
<input type="checkbox"/> Additional inventors are being named on the _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (280 characters max)					
MULTIFUNCTIONAL BLENDS FOR CONTROL OF GAS HYDRATE FORMATION					
Direct all correspondence to: CORRESPONDENCE ADDRESS					
<input checked="" type="checkbox"/> Customer Number <b>24923</b>					
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ENCLOSED APPLICATION PARTS (check all that apply)					
<input checked="" type="checkbox"/> Specification Number of Pages <b>20</b>		<input type="checkbox"/> CD(s), Number _____			
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<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76		Express Mail Certificate Return postcard			
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT					
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.		<input type="checkbox"/> A check or money order is enclosed to cover the filing fees		FILING FEE AMOUNT (\$)	
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: <b>02-0429</b>		<input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached		<b>160.00</b>	
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government					
<input checked="" type="checkbox"/> No.					
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Respectfully submitted

SIGNATURE

David L. Mossman

TYPED or PRINTED NAME

512/219-4026

TELEPHONE

Date 09 / 03 / 02

REGISTRATION NO.  
(if appropriate)  
Docket Number:

29,570

194-29360-P

## **USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT**

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:	:	<u>PATENT</u>
DANIEL L. CROSBY, et al.	:	
Serial No.:	:	
Filed:	:	Group Art Unit:
For: MULTIFUNCTIONAL BLENDS FOR	:	Examiner:
CONTROL OF GAS HYDRATE	:	Docket No.: 194-29360-P
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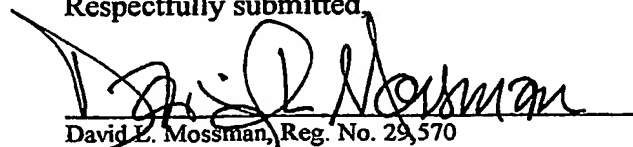
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DANIEL L. CROSBY, et al.  
 Respectfully submitted,

  
 David L. Mossman, Reg. No. 29,570

SEPTEMBER 3, 2002  
 Date

## MULTIFUNCTIONAL BLENDS FOR CONTROL OF GAS HYDRATE FORMATION

### Field of the Invention

**[0001]** The invention relates to methods and compositions for inhibiting the formation of hydrocarbon hydrates, and most particularly relates, in one non-limiting embodiment, to methods and compositions for inhibiting the formation of hydrocarbon hydrates during the production of oil and gas, where the compositions have more than one component.

### Background of the Invention

**[0002]** A number of hydrocarbons, especially lower-boiling light hydrocarbons, in formation fluids or natural gas are known to form hydrates in conjunction with the water present in the system under a variety of conditions – particularly at a combination of lower temperature and higher pressure. The hydrates usually exist in solid forms that are essentially insoluble in the fluid itself. As a result, any solids in a formation or natural gas fluid are at least a nuisance for production, handling and transport of the same. It is not uncommon for hydrate solids (or crystals) to cause plugging and/or blockage of pipelines or transfer lines or other conduits, valves and/or safety devices and/or other equipment, resulting in shutdown, loss of production and risk of explosion or unintended release of hydrocarbons into the environment either on-land or off-shore. Accordingly, hydrocarbon hydrates have been of substantial interest as well as concern to many industries, particularly the petroleum and natural gas industries.

**[0003]** Hydrocarbon hydrates are clathrates, and are also referred to as inclusion compounds. Clathrates are cage structures formed between a host molecule and a guest molecule. A hydrocarbon hydrate generally is composed of crystals formed by water host molecules surrounding the hydrocarbon guest molecules. The smaller or lower-boiling hydrocarbon molecules, particularly C<sub>1</sub> (methane) to C<sub>4</sub> hydrocarbons and their mixtures, are more problematic because it is believed that their hydrate or clathrate crystals are easier to form. For instance, it is possible for ethane to form

hydrates at as high as 4°C at a pressure of about 1 MPa. If the pressure is about 3 MPa, ethane hydrates can form at as high a temperature as 14°C. Even certain non-hydrocarbons such as carbon dioxide, nitrogen and hydrogen sulfide are known to form hydrates under the proper conditions.

5 [0004] There are two broad techniques to overcome or control the hydrocarbon hydrate problems, namely thermodynamic and kinetic. For the thermodynamic approach, there are a number of reported or attempted methods, including water removal, increasing temperature, decreasing pressure, addition of "antifreeze" to the fluid and/or a combination of these. Thermodynamic techniques function by  
10 shifting the hydrate formation equilibrium to a point outside the hydrate-forming conditions exhibited in the fluid. Kinetic inhibitors operate within hydrate equilibrium conditions. The kinetic approach generally attempts (a) to prevent the smaller hydrocarbon hydrate crystals from agglomerating into larger ones; (b) to inhibit the hydrocarbon hydrates from being formed in the first place; (c) to slow down crystal  
15 formation or growth under a particular set of conditions; and/or a combination of these approaches.

[0005] Kinetic efforts to control hydrates have included use of different materials as inhibitors. For instance, onium compounds with at least four carbon substituents are used to inhibit the plugging of conduits by gas hydrates. Additives such as  
20 polymers with lactam rings have also been employed to control clathrate hydrates in fluid systems. These kinetic inhibitors are commonly labeled Low Dosage Hydrate Inhibitors (LDHI) in the art.

[0006] Thus, it is desirable if new gas hydrate inhibitors are discovered which would yield comparable or improved results over known gas hydrate inhibitors.  
25

### Summary of the Invention

[0007] An object of the invention is to provide a method for inhibiting gas hydrate formation in mixtures of hydrate-forming guest molecules and water where hydrates would otherwise form to a greater extent in absence of the method.

30 [0008] Another object of the invention is to provide gas hydrate inhibitor compositions and/or hydrate inhibitor synergists that are readily produced. These

compositions may be blended with other oil field chemistries such as, but not limited to, corrosion, paraffin, scale and/or asphaltene inhibitors.

[0009] In carrying out these and other objects of the invention, there is provided, in one form, a method for inhibiting formation of hydrocarbon hydrates in a mixture  
5 that contains water and hydrate-forming guest molecules. The method involves contacting the mixture with a composition under conditions effective to form the hydrocarbon hydrates in the absence of the composition, where the composition has at least two of the following components: (1) at least one large molecular weight polymer having at least 1,000 atomic mass units (amu), (2) at least one  
10 small molecular weight species having less than 1,000 amu, and (3) at least one surfactant. The composition amount is effective in inhibiting formation of the hydrocarbon hydrates in the mixture.

[0010] In another non-limiting embodiment of the invention, in the method described immediately above, the large molecular weight polymer may be linear,  
15 branched and crosslinked polymers having at least one acyclic or cyclic pendant group containing from 3 to 7 carbon atoms, and these linear, branched and crosslinked polymers may contain one or more N, O, or S heteroatoms. The small molecular weight species may be polyethyleneimine, polyallylamine, starch, sugars, amines that contain 1 to 20 carbon atoms, alcohols that contain 1 to 20 carbon  
20 atoms, and/or polymers or copolymers of vinyl alcohol or allyl alcohol. These small molecular weight species may also may also be modified to have at least one acyclic or cyclic pendant group containing from 3 to 7 carbon atoms, and these small molecular weight species may be substituted with one or more N, O, or S heteroatoms. The surfactant may be a cationic, anionic or nonionic surfactant from  
25 the group of polyoxyethylene ethers, sorbitans, long chain alcohols, sulfates, diols, fatty acids, quaternary amines and mixtures thereof.

[0011] In another aspect, the invention includes hydrate-inhibited mixtures formed by the method described above. Additionally, the invention concerns compositions having (1) at least one large molecular weight polymer having at least 1,000 atomic  
30 mass units (amu), (2) at least one small molecular weight species having less than 1,000 amu, and (3) at least one surfactant.

### Detailed Description of the Invention

[0012] In the present invention there are included methods and compositions used therein for inhibiting, retarding, mitigating, reducing, controlling and/or delaying  
5 formation of hydrocarbon hydrates or agglomerates of hydrates. The method may be applied to prevent or reduce or mitigate plugging of conduits, pipes, transfer lines, valves, and other places or equipment where hydrocarbon hydrate solids may form under conditions conducive to their formation or agglomeration. In one aspect of the invention, unexpected, synergistic results in inhibiting hydrate formation may  
10 be obtained.

[0013] The term "inhibiting" is used herein in a broad and general sense to mean any improvement in preventing, controlling, delaying, reducing or mitigating the formation, growth and/or agglomeration of hydrocarbon hydrates, particularly light hydrocarbon gas hydrates in any manner, including, but not limited to kinetically,  
15 thermodynamically, by dissolution, by breaking up, other mechanisms, or any combination thereof. Although the term "inhibiting" is not intended to be restricted to the complete cessation of gas hydrate formation, it may include the possibility that formation and/or agglomeration of any gas hydrate is entirely prevented.

[0014] The terms "formation" or "forming" relating to hydrates are used herein in a  
20 broad and general manner to include, but are not limited to, any formation of hydrate solids from water and hydrocarbon(s) or hydrocarbon and non-hydrocarbon gas(es), growth of hydrate solids, agglomeration of hydrates, accumulation of hydrates on surfaces, any deterioration of hydrate solids plugging or other problems in a system and combinations thereof.

25 [0015] In brief, the invention concerns a methodology of controlling (*i.e.* preventing, retarding, and/or anti-agglomeration) gas hydrates to facilitate fluid transportation and handling. In one non-limiting embodiment of the invention, a tri-functional gas hydrate inhibitor formulation is involved. This formulation is a blend of large molecular weight polymer(s) having a molecular weight of 1,000 amu or  
30 greater, combined with small molecular weight hydrocarbons or species having a molecular weight less than 1,000 amu, with surfactants. The large and small

molecular weight components act as hydrate crystal nucleation and/or crystal growth inhibitors while the surfactant is a solvating and/or surface tension modifier. Collectively, the three components act synergistically to control hydrate formation. That is, in one non-limiting aspect of the invention, when combinations of the  
5 components are used together, results can be obtained that are more than additive as compared with the results shown when the individual components are used alone.

[0016] The present method is useful for inhibiting hydrate formation for many hydrocarbons and hydrocarbon and/or non-hydrocarbon mixtures. The method is  
10 particularly useful for lighter or low-boiling, C<sub>1</sub>-C<sub>5</sub> hydrocarbon gases, non-hydrocarbon gases or gas mixtures at ambient conditions. Examples of such gases include, but are not necessarily limited to, methane, ethane, ethylene, acetylene, propane, propylene, methylacetylene, n-butane, isobutane, 1-butene, trans-2-butene, cis-2-butene, isobutene, butene mixtures, isopentane, pentenes, natural  
15 gas, carbon dioxide, hydrogen sulfide, nitrogen, oxygen, argon, krypton, xenon, and mixtures thereof. Other examples include various natural gas mixtures that are present in many gas and/or oil formations and natural gas liquids (NGL). The hydrates of all of these low-boiling hydrocarbons are also referred to as gas hydrates. The hydrocarbons may also comprise other compounds including, but not  
20 limited to CO, CO<sub>2</sub>, COS, hydrogen, hydrogen sulfide (H<sub>2</sub>S), and other compounds commonly found in gas/oil formations or processing plants, either naturally occurring or used in recovering/processing hydrocarbons from the formation or both, and mixtures thereof. In one non-limiting embodiment of the invention, the surfactant is optional in the composition.

25 [0017] When an effective amount is used, hydrocarbon hydrate formation is inhibited under conditions where such hydrate formation is not otherwise inhibited in the absence of such effective amount. After the contacting and after the conditions no longer favor formation of gas hydrates, the method may further comprise, optionally, removing the composition, individual or certain components of the  
30 composition or other compounds or mixtures in the composition or the mixture comprising water and the hydrate-forming guest molecules.



**[0018]** The large molecular weight component of the present inventive composition involves linear, branched and crosslinked polymers having at least one acyclic or cyclic pendant group containing from 3 to 7 carbon atoms, as well as these linear, branched and crosslinked polymers containing at least one N, O, and/or S heteroatom. More specific examples of suitable large molecular weight components include, but are not necessarily limited to, branched dendrimers, hyperbranched molecules, polymers and copolymers of vinylpyrrolidone, polymers and copolymers of vinylcaprolactam, reaction products of polyamines with formaldehyde and an amide, reaction products of polyamides with formaldehyde and an amine, n-vinyl-n-methyl acetamide (VIMA), vinylcaprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylate terpolymer (GAFFIX® VC-173 terpolymer available from International Specialty Products), and mixtures thereof. Suitable branched dendrimers include, but are not necessarily limited to, ASTRAMOL™ poly(propylene imine) dendrimers available from DSM. Suitable hyperbranched molecules include, but are not necessarily limited to, HYBRANE™ hyperbranched polyesteramides being developed by DSM.

**[0019]** The large molecular weight polymers may be reaction products of an amine or a polyamine with an aldehyde together with an amide or a polyamide. Also, the large molecular weight polymers may be reaction products of an alcohol or polyalcohol with an aldehyde together with an amide or polyamide. In addition, the large molecular weight polymers may be reaction products of an alcohol or polyhydroxy compound with an aldehyde together with an amine or polyamine.

**[0020]** In one non-limiting embodiment of the invention, suitable amines to make the large molecular weight reaction product include, but are not necessarily limited to, primary or secondary cyclic amines, primary or secondary acyclic amines, fatty alkyl amines, polyalkyleneimines, polyallylamines, polyamines derived from condensation of ethylenedichloride, epichlorohydrin, or diepoxide with ammonia, ethylenediamine, polyethylenediamine, hexamethylenediamine, bis(hexamethylene)triamine, and mixtures thereof. More specifically, acceptable non-polymeric amines may include, but are not necessarily limited to, N-methylbutylamine, and cyclic or acyclic amines containing from 2 to 14 carbon

- atoms. The amine may be primary or secondary. The amines and polyamines as defined herein may also be substituted with oxygen atoms, such as in the case of morpholine, or may be substituted with tertiary nitrogen atoms, such as in the case of imidazole or bis(dimethylamino)dipropylamine. Other particular, suitable amines
- 5 include fatty alkyl amines, fatty alkyl diamines (e.g. N-tallowalkyl-1,3-diaminopropane such as Duomeen T available from Akzo Nobel), and higher derivatives such as fatty alkyl triamines. Additional equivalents may also include, but are not necessarily limited to, polyether amines sold under the trade name Jeffamine by Huntsman Chemical or ether amines sold by Tomah Products.
- 10 Acceptable functional equivalents of the polyamine may include, but are not necessarily limited to, polypropyleneimine, polyallylimine, and polyamines derived from the condensation of ethylene dichloride, epichlorohydrin or diepoxides with ammonia, ethylenediamine, higher ethyleneamines, hexamethylenediamine, bis(hexamethylene)triamine, and mixtures thereof. In one particular, non-limiting
- 15 embodiment of the invention, the preferred polyamine is polyethyleneimine.
- [0021]** With respect to alcohols and polyalcohols, substances suitable for the reaction product include alcohols and diols containing 1 to 20 carbon atoms, starch, sugars, and polymers and/or copolymers of vinyl alcohol or allyl alcohol.
- [0022]** With respect to the aldehydes, the aldehydes suitable for the reaction
- 20 product include, but are not necessarily limited to, aldehydes and dialdehydes having from 1 to 8 carbon atoms and compounds capable of generating these aldehydes under conditions effective to form the reaction product. In a particularly preferred, but non-limiting embodiment of the invention, the aldehyde is formaldehyde and compounds capable of generating formaldehyde, such as
- 25 paraformaldehyde.
- [0023]** With respect to the amides or polyamides used to form the large molecular weight polymer reaction products, such amide or polyamide may include, but is not necessarily limited to, cyclic amides such as caprolactam, acyclic amides, polyacrylamide, and mixtures thereof. Functional equivalents of caprolactam may
- 30 include, but are not necessarily limited to, cyclic secondary lactams or acyclic primary and/or secondary amides and mixtures thereof. The suitable lactams may

contain from 3 to 10 carbon atoms and preferably 4 to 6 carbon atoms, in non-limiting embodiments. Suitable acyclic amides may contain 1 to 12 carbon atoms and preferably from 3 to 8 carbon atoms. Functional equivalents of suitable polyacrylamides include, but are not necessarily limited to, polymethacrylamide, polymaleimide, copolymers of maleimide, condensation polymers of amino acids (or the corresponding cyclic lactam or cyclic dimer), condensation polymers derived from dicarboxylic acids and diamines, and mixtures thereof. In one non-limiting embodiment of the invention, it is preferred that the amide be caprolactam, and in another non-limiting embodiment of the invention, it is preferred that the polyamide be aqueous polyacrylamide.

**[0024]** In a first non-limiting embodiment of the invention, the large molecular weight polymers of this invention are made by the reaction of a polyamine (such as polyethyleneimine) with an aldehyde (such as formaldehyde) and an amide that may be cyclic or amide, where these three reactants are defined as above. In a second non-limiting embodiment of the invention, the large molecular weight polymers of this invention are made by the reaction of a polyamide (such as polyarylamide) with an aldehyde (such as formaldehyde) and an amine, where these three reactants are defined as above. In a third non-limiting embodiment of the invention, the inventive large molecular weight polymers are made by the reaction of an amine containing a hydrophobic group, such as a fatty alkyl amine (or fatty alkyl diamine or fatty alkyl triamine) with an aldehyde (such as formaldehyde) and an amide that may be cyclic or amide, where these three reactants are defined as above. In this case, the resulting product has both hydrophilic and hydrophobic regions. In one non-limiting embodiment of the invention, it is preferred not to react polyamines with polyamides and aldehydes as the expected reaction products from this reaction may be too complex or a too high molecular weight solid to be of use, and because of the complexity of formulating practical high viscosity fluids for injection through small diameter conduits such as an umbilical.

**[0025]** Some of the large molecular weight polymers of this invention may be formed by reacting the amine or polyamine, or alcohol or polyalcohol with the aldehyde and the amide or polyamide in molar ratios of from about 1:0.01:0.01 to

about 1:100:100; preferably from about 1:0.1:0.1 to about 1:1:1. The reaction conditions for producing the reaction products of this invention are relatively mild, ranging from about 15 to about 150°C, preferably from about 65 to about 120°C. The reaction pressures to make these products range from about 10 to about 1000 kPa, preferably from about 50 to about 500 kPa.

[0026] The small molecular weight species are polymers or non-polymers having less than 1,000 amu. They include, but are not necessarily limited to, polyethyleneimines, polyallylamines, amines that contain 1 to 20 carbon atoms, alcohols that contain 1 to 20 carbon atoms, starch, sugars, and polymers and/or copolymers of vinyl alcohol or allyl alcohol. The small molecular weight species may also be modified to also contain at least one acyclic or cyclic pendant group containing from 3 to 7 carbon atoms. Also included are the above small molecular weight species containing N, O, and/or S heteroatom.

[0027] Suitable surfactants for use in the inventive compositions include, but are not necessarily limited to cationic, anionic or nonionic surfactants that may be polyoxyethylene ethers, sorbitans, long chain alcohols, sulfates, diols, fatty acids, quaternary amines and mixtures thereof. Suitable specific surfactants include, but are not necessarily limited to, RE4136HIW, RE4154HIW and RE4394HIW sold by Baker Petrolite Corporation.

[0028] With respect to the proportions of the various components of the inventive composition, for any two unique large molecular weight polymer and different small molecular weight species, there is an optimum molar ratio between the two. However, the optimum molar ratio is dependent upon a number of complex, interrelated factors and will vary. These factors include, but are not necessarily limited to, the nature of the components, the components in the fluid system being treated, the temperature and pressure in the fluid system being treated and the like. Nevertheless, in order to give some idea of component proportions that might be used, the composition may comprise from about 0.1 to about 2 wt% of the at least one large molecular weight polymer having at least 1,000 amu; from about 0.1 to about 2 wt% of the at least one small molecular weight species having less than 1,000 amu; and from about 10 to about 3000 ppm of the at least one surfactant. In

a non-limiting, preferred embodiment of the invention, the composition comprises from about 0.5 to about 1 wt% of the at least one large molecular weight polymer having at least 1,000 amu; from about 0.5 to about 1 wt% of the at least one small molecular weight species having less than 1,000 amu; and from about 50 to about 5 1000 ppm of the at least one surfactant. In one non-limiting embodiment of the invention, the concentration of surfactant is 2% by weight or less in the treated fluid. In a preferred embodiment of the invention, the surfactant is applied at relatively low concentrations, on the order of 0.1 wt% or less. The surfactant's applied concentration is also dependent on the composition of the fluid being treated and its 10 conditions, and will vary accordingly.

**[0029]** The contacting may be achieved by a number of ways or techniques, including, but not necessarily limited to, mixing, blending with mechanical mixing equipment or devices, stationary mixing setup or equipment, magnetic mixing or other suitable methods, other equipment and means known to one skilled in the art 15 and combinations thereof to provide adequate contact and/or dispersion of the composition in the mixture. The contacting can be made in-line or offline or both. The various components of the composition may be mixed prior to or during contact, or both. As discussed, if needed or desired, the composition or some of its components may be optionally removed or separated mechanically, chemically, or 20 by other methods known to one skilled in the art, or by a combination of these methods after the hydrate formation conditions are no longer present.

**[0030]** Because the present invention is particularly suitable for lower boiling hydrocarbons or hydrocarbon and/or non-hydrocarbon gases at ambient conditions with no more than five carbon atoms, the pressure of the hydrate-forming condition 25 is usually at or greater than atmospheric pressure (*i.e.* greater than or equal to about 101 kPa), preferably greater than about 1 MPa, and more preferably greater than about 5 MPa. The pressure in certain formations or processing plants or units could be much higher, say greater than about 20 MPa. There is no specific high pressure limit. The present method can be used at any pressure that allows 30 formation of hydrocarbon gas hydrates.

[0031] The temperature of the condition for contacting is usually below, the same as, or not much higher than the ambient or room temperature. Lower temperatures tend to favor hydrate formation, thus requiring the treatment with the compositions of the present invention. At much higher temperatures, however, hydrocarbon  
5 hydrates may not form, thus obviating the need of carrying out any treatments.

[0032] It will be appreciated that it is very difficult, if not impossible, to predict in advance the proportions effective in inhibiting hydrocarbon hydrate formations in any given situation. There are a number of complex, interrelated factors that must be taken into account in determining the effective dosage or proportion, including,  
10 but not necessarily limited to, the proportion of water in the hydrocarbon, the nature of the hydrocarbon, the temperature and pressure conditions that the mixture of hydrocarbon and water are subject to, the particular hydrocarbon hydrate inhibitor employed, etc. Nevertheless, in the interest of attempting to provide some general guidance of effective proportions, relative to the water phase, the amount of the  
15 reaction product is preferably less than about 3 wt%, preferably less than about 2 wt%, but is limited only by what is economically feasible.

[0033] In addition to the components of the inventive composition discussed above, the hydrocarbon inhibitor composition may further comprise other additional components, including, but not limited to, different controlling chemistries such as  
20 corrosion, wax, asphaltene and other hydrate inhibitors and/or solvents. These other chemistries should not conflict with the use of the hydrate formation-inhibiting compositions of the present invention. Suitable solvents include, but are not limited to water; at least one oxygenated compound selected from C<sub>1</sub>-C<sub>6</sub> alcohols, C<sub>2</sub>-C<sub>6</sub> glycols, C<sub>1</sub>-C<sub>6</sub> mono-aliphatic, preferably mono-alkyl, ethers of C<sub>2</sub>-C<sub>6</sub> glycol,  
25 glycerin, C<sub>1</sub>-C<sub>6</sub> mono-aliphatic, particularly mono-alkyl, ethers of glycerin, C<sub>1</sub>-C<sub>6</sub> di-aliphatic, particularly dialkyl, ethers of glycerin, glycerin esters of C<sub>1</sub>-C<sub>6</sub> carboxylate; tetrahydrofuran; N-methylpyrrolidone; sulfolane; C<sub>3</sub>-C<sub>10</sub> ketones, and mixtures thereof. Examples of preferred solvents include water and liquid oxygenated materials such as methanol, ethanol, propanol, glycols like ethylene glycol, 1,2-  
30 propylene glycol, 1,3-propylene glycol, glycerin, esters and ethers of glycerin, CELLOSOLVE® (2-ethoxyethanol), CELLOSOLVE derivatives, 2-methoxyethanol,

ethoxylated propylene glycols, ketones such as cyclohexanone and diisobutylketone, and mixtures thereof. The solvent is present in the total hydrocarbon hydrate inhibiting composition in the range of from 0% to about 85%, preferably from about 0% to about 65%, of the total composition, based on volume.

5 CELLOSOLVE is a registered trademark of Union Carbide Corporation.

[0034] Because some of the reaction products disclosed herein are solids under ambient conditions, it is often preferred to use a suitable solvent as described above in the composition. This allows the formation of a homogeneous or uniform solution, suspension, emulsion or a combination of these, of all the components for  
10 easier mixing or distributing or dispersing the composition in the hydrocarbon/water fluid or system to be treated. As a result, more efficient and/or favorable contacting of the composition with the mixture comprising water and the hydrate-forming guest molecules can be effected.

[0035] The present invention also may be used in combination with other methods  
15 or processes, which have been known to one skilled in the art as discussed in the background to help inhibit formation of hydrates.

[0036] The following examples only illustrate certain specific embodiments of the invention. They are not meant to limit the spirit or scope of the present invention in any manner. When the example and the associated results are read together with  
20 the rest of the written description of specification and the claims, one skilled in the art will more appreciate and better understand the instant invention and its other embodiments.

#### Experimental Set-up

25 [0037] All testing is isochoric. This results in the cell pressure dropping as the cell temperature is ramped from 72°F to 40°F. The starting pressure is about 1500 psig, the final cell pressure at 40°F, before hydrate formation, varies, and is dependent on the test fluids (composition, liquid hydrocarbon ratio, etc.) employed. Generally, the cell pressure drops to the 1200 to 1300 psig range before hydrate formation.

**[0038]** Testing is performed with a bank of modified sight flow indicators, which serve as pressure vessel reactors. Each reactor or cell is isolated from its companions, and is independently pressurized and contains its own, independent pressure transducer. Up to six reactors constitute a bank of test cells. A test is performed by immersing a bank of test cells in a common temperature controlled water bath.

**[0039]** Depending upon the experimental protocol, the water bath (and therefore the cells within) is gently rocked and/or held stationary at time intervals. Stationary intervals are designed to mimic pipeline shut-ins.

**[0040]** Other important procedural features include:

1. The bath water temperature and each pressure transducer are independently monitored and the data preserved by a computerized data acquisition system.
2. Each cell contains stainless steel ball(s) that provide agitation of the cell's contents when the water bath is rocked.
3. At least one cell in every test bank is a control, containing either a reference inhibitor or none at all.
4. Tests employ either the shock cool method wherein the cells are placed in pre-chilled water or are ramp cooled from near room temperature to some target low temperature.
5. All cells are disassembled and meticulously cleaned with a proprietary system of solvents between each test.
6. Multiple repeats of a particular inhibitor blend are often made to provide a statistical sampling of a blend's performance.
7. Each cell has a window for visual observations.
8. Visual observations are made at irregular intervals to better ascertain the processes occurring within the cell and to confirm the results of the pressure data.

**[0041]** For the purpose of kinetic hydrate testing, the life and failure of a test blend is measured as the time expended before radical hydrate formation (retention time



or time to failure). This point is denoted by a drop in pressure that is independent of a pressure drop due to a change in temperature.

[0042] The results of multiple experiments validating this invention are presented in the following Tables.

5

**TABLE I**

<u>Ex.</u>	<u>Test Blend</u>	<u>approx. wt% LDHI in Brine</u>	<u>Induction Time (hr)<sup>1</sup></u>
1	Blank	0	11.7
2	RE4890 <sub>HIW</sub>	1	13.0
3	HA 1690	1	15.5
4	HA1690 + RE4890 <sub>HIW</sub>	1	16.0
5	HA1690 + RE4890 <sub>HIW</sub> + RE4394 <sub>HIW</sub>	1	25.5

<sup>1</sup> Using a synthetic natural gas blend containing methane, ethane, propane & carbon dioxide (1/5/5.4/88.6 mole% CO<sub>2</sub>/C<sub>2</sub>/C<sub>3</sub>/C<sub>1</sub>) and 80/20 vol% brine/black oil solution

- 10 HA1690 = a >1000 amu hybrane LDHI  
 RE4890<sub>HIW</sub> = a modified 600 amu PEI  
 RE4394<sub>HIW</sub> = a quaternary amine (surfactant)

**TABLE II**

<u>Ex.</u>	<u>Test Blend</u>	<u>LDHI approx. wt%</u>	<u>RE4394 HIW approx. ppm as supplied</u>	<u>Induction Time (hr)<sup>1</sup></u>
6	Blank	0	0	11.7
7	HA1690 + RE4890 <sub>HIW</sub>	1	0	16.0
8	HA1690 + RE4890 <sub>HIW</sub> + RE4394 <sub>HIW</sub>	1	300	25.5
9	HA1690 + RE4890 <sub>HIW</sub> + RE4394 <sub>HIW</sub>	1	625	19.9
10	HA1690 + RE4890 <sub>HIW</sub> + RE4394 <sub>HIW</sub>	1	1250	18.4
11	HA1690 + RE4890 <sub>HIW</sub> + RE4394 <sub>HIW</sub>	1	4975	13.3
12	HA1690 + RE4890 <sub>HIW</sub> + RE4394 <sub>HIW</sub>	1	7450	14.5
13	HA1690 + RE4890 <sub>HIW</sub> + RE4394 <sub>HIW</sub>	1	9900	14.3

<sup>1</sup> Using a synthetic natural gas blend containing methane, ethane, propane & carbon dioxide and 80/20 vol% brine/black oil solution; the brine used was 2.5 wt% brine with 10 wt% MeOH

- 5 [0043] Many modifications may be made in the compositions and methods of this invention without departing from the spirit and scope thereof that are defined only in the appended claims. For example, the exact components and their proportions may be different from those used here. Various combinations of large molecular weight polymers with small molecular weight species and surfactants other than
- 10 those exemplified here are also expected to find use in providing improved hydrate inhibitors. Further, different reaction products from those discussed and exemplified are also expected to be useful herein.

### Claims

**We Claim:**

**1. A method for inhibiting formation of hydrocarbon hydrates in a mixture comprising water and hydrate-forming guest molecules, the method comprising contacting the mixture with a composition under conditions effective to form the hydrocarbon hydrates in the absence of the composition, where the composition comprises at least two of the following components:**

**at least one large molecular weight polymer having at least 1,000 atomic mass units (amu);**

**at least one small molecular weight species having less than 1,000 amu; and  
at least one surfactant,**

**and where the composition amount is effective in inhibiting formation of the hydrocarbon hydrates in the mixture.**

**2. The method of claim 1 where the large molecular weight polymer is selected from the group consisting of linear, branched and crosslinked polymers having at least one acyclic or cyclic pendant group containing from 3 to 7 carbon atoms, and said linear, branched and crosslinked polymers also containing a heteroatom selected from the group consisting of N, O, and S, and mixtures thereof.**

**3. The method of claim 2 where the large molecular weight polymer is selected from the group consisting of branched dendrimers, hyperbranched molecules, polymers and copolymers of vinylpyrrolidone, polymers and copolymers of vinylcaprolactam, reaction products of polyamines with formaldehyde and an amide, reaction products of polyamides with formaldehyde and an amine, n-vinyl-n-methyl acetamide (VIMA), vinylcaprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylate terpolymer, and mixtures thereof.**

**4. The method of claim 1 where the small molecular weight species is selected from the group consisting of polyethyleneimine, polyallylamine, amines that contain**

1 to 20 carbon atoms, alcohols that contain 1 to 20 carbon atoms, starch, sugars, and/or polymers or copolymers of vinyl alcohol or allyl alcohol that also may be modified to contain at least one acyclic or cyclic pendant group also containing from 3 to 7 carbon atoms, and said small molecular weight species containing a heteroatom selected from the group consisting of N, O, and S, and mixtures thereof.

5. The method of claim 1 where the surfactant is a cationic, anionic or nonionic surfactant selected from the group consisting of polyoxyethylene ethers, sorbitans, long chain alcohols, sulfates, diols, fatty acids, quaternary amines and mixtures thereof.

6. The method of claim 1 where the composition comprises  
from about 0.1 to about 2 wt% of the at least one large molecular weight polymer having at least 1,000 amu;  
from about 0.1 to about 2 wt% of the at least one small molecular weight species having less than 1,000 amu; and  
from about 10 to about 3000 ppm of the at least one surfactant.

7. The method of claim 1 where the hydrate-forming guest molecules are selected from the group consisting of methane, ethane, ethylene, acetylene, propane, propylene, methylacetylene, n-butane, isobutane, 1-butene, trans-2-butene, cis-2-butene, isobutene, butene mixtures, isopentane, pentenes, natural gas, carbon dioxide, hydrogen sulfide, nitrogen, oxygen, argon, krypton, xenon, and mixtures thereof.

8. A composition for inhibiting formation of hydrates where the composition comprises:  
at least one large molecular weight polymer having at least 1,000 atomic mass units (amu);  
at least one small molecular weight species having less than 1,000 amu; and

at least one surfactant.

9. The composition of claim 8 where the large molecular weight polymer is selected from the group consisting of linear, branched and crosslinked polymers having at least one acyclic or cyclic pendant group containing from 3 to 7 carbon atoms, and said linear, branched and crosslinked polymers also containing a heteroatom selected from the group consisting of N, O, and S, and mixtures thereof.

10. The composition of claim 8 where the large molecular weight polymer is selected from the group consisting of branched dendrimers, hyperbranched molecules, polymers and copolymers of vinylpyrrolidone, polymers and copolymers vinylcaprolactam, reaction products of polyamines with formaldehyde and an amide, reaction products of polyamines with formaldehyde and an alcohol, reaction products of polyamides with formaldehyde and an amine, n-vinyl-n-methyl acetamide (VIMA), vinylcaprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylate terpolymer, and mixtures thereof.

11. The composition of claim 8 where the small molecular weight species is selected from the group consisting of polyethyleneimine, polyallylamine, amines that contain 1 to 20 carbon atoms, alcohols that contain 1 to 20 carbon atoms, starch, sugars, and/or polymers or copolymers of vinyl alcohol or allyl alcohol that also may be modified to contain at least one acyclic or cyclic pendant group containing from 3 to 7 carbon atoms, and said small molecular weight species also containing a heteroatom selected from the group consisting of N, O, and S, and mixtures thereof.

12. The composition of claim 8 where the surfactant is a cationic, anionic or nonionic surfactant selected from the group consisting of polyoxyethylene ethers, sorbitans, long chain alcohols, sulfates, diols, fatty acids, quaternary amines and mixtures thereof.

13. The composition of claim 8 where the composition comprises  
from about 0.1 to about 2 wt% of the at least one large molecular weight  
polymer having at least 1,000 amu;  
from about 0.1 to about 2 wt% of the at least one small molecular weight  
species having less than 1,000 amu; and  
from about 10 to about 3000 ppm of the at least one surfactant.
14. A hydrate inhibited mixture comprising:  
water,  
hydrate-forming guest molecules, and  
a composition comprising:  
at least one large molecular weight polymer having at least  
1,000 atomic mass units (amu);  
at least one small molecular weight species having less than  
1,000 amu; and  
at least one surfactant,  
where the composition is present in a concentration effective to inhibit  
hydrate formation in the mixture.
15. The hydrate inhibited mixture of claim 14 where the hydrate-forming guest  
molecules are selected from the group consisting of methane, ethane, ethylene,  
acetylene, propane, propylene, methylacetylene, n-butane, isobutane, 1-butene,  
trans-2-butene, cis-2-butene, isobutene, butene mixtures, isopentane, pentenes,  
natural gas, carbon dioxide, hydrogen sulfide, nitrogen, oxygen, argon, krypton,  
xenon, and mixtures thereof.

## MULTIFUNCTIONAL BLENDS FOR CONTROL OF GAS HYDRATE FORMATION

### Abstract of the Disclosure

A method for inhibiting formation of hydrocarbon hydrates in mixtures of water and a hydrate-forming guest molecule has been discovered that involves adding a composition to the mixtures in an amount that is effective in inhibiting formation of the hydrocarbon hydrates under conditions otherwise effective to form the hydrocarbon hydrates in the absence of the reaction product. The composition includes both a large molecular weight polymer and a different, small molecular weight species, and optionally a surfactant. In one aspect of the invention, the combination of the large molecular weight polymer and a different, small molecular weight species may give synergistic results.